

December, 1882), sets up two baro-manometers, one on the (low) ground, the other at the top of a high building, or of a hill. The manometric branches are connected by means of a long metallic tube. On rarefying the air in the tube through an adjutage adapted near one of the manometers, the rarefaction is propagated towards the other, but owing to gravity, the lower one always shows a greater pressure than the other. By varying the conditions, the hypsometric formula may be established directly. To ascertain whether gases have or have not a limit of elasticity, two baro-manometers are placed below and connected by separate tubes with the one above. On rarefying through a tube near one of the lower manometers, a limit is reached at which gravity prevents the air of the latter manometer from rising, and it remains stationary while the other continues to fall, if the limit of elasticity exist. The author was fitting up his apparatus for these experiments on a very high old building at St. Petersburg.

In another paper to the same Society (*loc. cit.*), M. Piltchikoff describes an arrangement for measuring the refractive index of liquids of which one has but small quantities. A hollow lens is filled with the liquid, and with the aid of a graduated scale and a microscope, one measures exactly the focal distance of a monochromatic flame placed at a given distance from the lens. The author gives a simple formula for calculating the index of the liquid, when the constants of the apparatus have been determined once for all. In one set of experiments, the index of glycerine was found = 1.47298, with a probable error estimated at ± 0.00001 .

In the common practice of referring the electromotive force of galvanic combinations to the Daniell element as unit, some difficulty and confusion have arisen from differences in the construction of that element by different physicists. In a recent investigation of this matter (*Wied. Ann.*, 13, 1882), Herr Kittler gives the name of "normal element" to a combination, which is as follows:—Amalgamated, chemically pure zinc, in dilute sulphuric acid of specific gravity 1.075 at 18° C.; and chemically pure copper in concentrated copper sulphate solution of specific gravity 1.190 to 1.200. He finds that the electromotive force of the Daniell element (Zn , H_2SO_4 , CuSO_4 , Cu) increases with percentage proportion of the acid to a maximum occurring at the same place, whether the copper sulphate solution be concentrated or dilute, viz. with 25 to 30 per cent. of the acid; with further hydration of the acid there is decrease. The increase is greater, however, the more dilute the CuSO_4 solution used, and greatest with pure water. It is further found that, if very weak acids are used, there is decrease of the electromotive force with dilution of the copper-sulphate solution. Accordingly, there is a degree of concentration of the acid, with which a Daniell element furnishes the same tension, whether the CuSO_4 be concentrated or diluted to any extent. The solution in question has the specific gravity 1.0011 at 16° C., and is compounded of 750 ccm. H_2O and 100 ccm. dilute H_2SO_4 of sp. gr. 1.007. Herr Kittler compares the action of his "normal element" with that of other practical units.

In a recent paper to the Vienna Academy (*Wied. Ann.*, 13, 1882), Prof. Stephan describes an investigation of the magnetic screening action (*Schirmwirkung*) of iron (which is exemplified in Thomson's marine galvanometer and the Gramme machine). His experiments were made with hollow iron cylinders and iron rings, and were of three kinds, viz. deflection, oscillation, and induction.

THE sound-vibrations of solid bodies (glass cylinders) in contact with liquids has been lately studied by Herr Auerbach (*Wied. Ann.*, No. 13, 1882). He finds that the *geometrical lowering of tone*, represented by the ratio of the vibration number (n_0) of the empty vessel to that of the same vessel filled with water (n), is smaller the higher the tone of the empty vessel, and greater the narrower the vessel. The *arithmetical lowering of tone* (represented by $(n_0 - n)/n_0$) in a vessel of mean pitch, is inversely proportional to the square root of the vibration-number of the empty glass, and (approximately) to that of the number of wave-lengths which the sound of the empty vessel traverses from the wall to the axis. In glasses of different width it is (approximately) inversely proportional to the square root of the width. The specific lowering of tone of a liquid depends primarily on the density, and is greater, the greater this is, though it does not increase so quickly; next, on the compressibility, being greater the smaller this is.

AN INQUIRY INTO THE DEGREE OF SOLUBILITY REQUISITE IN MANURES, WITH SPECIAL REFERENCE TO PRECIPITATED CALCIC AND MAGNESIC PHOSPHATES

SOME remarkable field trials, recently conducted in Scotland by Jamieson and others, have tended to raise serious doubts concerning the correctness of the high relative values, hitherto assigned by chemists to dissolved phosphates, commonly termed super-phosphates, for manurial purposes. We propose, therefore, to examine briefly the action of phosphates in the soil; the conditions under which they become available for the nutrition of plants, and the degree of solubility which, considering these facts, would appear to be most advantageous for the purposes of the agriculturist. We hope to be able to show the great value of precipitated calcic and magnesian phosphates as manure-ingredients, and to assign some reasons for the comparative neglect which the salts of magnesia have hitherto received from agricultural chemists.

The careful and elaborate series of experiments undertaken by Dr. Voelcker respecting the "solubility of phosphatic materials" may be said to constitute the basis of our present inquiry, as the behaviour of phosphates in water is perhaps the readiest test of their activity as manures. Dr. Voelcker ascertained that one gallon of distilled water will dissolve the following amount of calcic phosphates, derived from the sources quoted:—

	Per gallon.
Estremadura phosphorite...	0.10 grains.
Norwegian apatite ...	0.44 "
Coprolites (mean of Suffolk and Cambridgeshire) ...	0.62 "
Monk's Island phosphate ...	1.00 "
Pure bone ash (from very hard bone) ...	1.18 "
Pure tribasic phosphate of lime, precipitated, burnt and finely ground ...	2.20 "
Guano ...	2.52 "
Pure tribasic phosphate, precipitated and still moist ...	5.56 "

The general deductions arrived at from these experiments, made about fifteen years ago, were that the phosphates in coprolites, apatite, and other phosphatic minerals were very little acted upon by water, and that "for agricultural purposes phosphatic minerals, as well as bone ash, should be treated with a quantity of sulphuric acid sufficient to convert the whole of the insoluble phosphates, therein contained, as completely as possible into soluble combinations. It is a waste of good raw materials to leave much of the insoluble phosphates unacted upon by acid." Broadly speaking, the above may be said to constitute the creed of the agricultural chemist at the present day, and the farmer buys his manure at a relatively high price, per unit of soluble phosphate.

On applying manures containing dissolved phosphates to the soil, nearly the whole of the phosphoric acid is at once neutralised by the various salts present therein, be they lime, alumina, or iron, and the chemist assures us that the superior estimation in which soluble salts are held arises from the property possessed by these salts of becoming rapidly diffused through the soil and precipitated therein, in an extremely fine state of sub-division. Voelcker, in some recent observations on this question, lays down certain propositions which are thus set forth in the abstract of the *Journal of the Chemical Society*, vol. xi. (1881) p. 640. These appear to us to state very clearly and briefly the accepted theories respecting the action of phosphates in manure.

1. Phosphates are not readily taken up by plants in a soluble form, but must be returned to an insoluble condition before they yield their useful properties.

2. The efficacy of insoluble calcium phosphate corresponds with the minuteness of division in which it is found in a manure.

3. The finer the particles in a phosphatic material, the easier it is dissolved in water, and the more energetic its action as a manure. Coarsely-ground coprolites and other minerals are less useful than the same materials in fine powder.

4. Calcium phosphate in porous soft bones is more soluble and energetic than in hard bones, and is more available in bone meal than in crushed bones.

5. Calcium phosphate in crystallised mineral phosphates—Norwegian, Canadian, and Spanish apatites, for example—is less

soluble and energetic than the same amount contained in porous phosphatic materials, such as certain descriptions of phosphoguanos.

6. Treatment with acids renders the material completely soluble in water, and the so-formed superphosphate, when put into the ground, is precipitated in a very fine state of division.

7. In the precipitated state the insoluble phosphate is immeasurably more finely divided than it could be obtained by mechanical means, and is consequently more energetic than any raw material mechanically ground.

8. The author's conclusion is that the chemical treatment with acid is the cheapest and best way of rendering mineral phosphates useful for agricultural purposes.

We think that it will be generally admitted that these propositions give a very reasonable statement of the case; but for the purposes of our inquiry we must supplement them with the following additional proposition. This has reference to a matter which has escaped the attention of Dr. Voelcker, but which is strongly supported by the results of the numerous recently-recorded practical trials.

"By reprecipitating the acid in a super-phosphate previous to its employment for agriculture by means of a suitable base, it becomes possible to obtain a neutral phosphate, possessed of a sufficient degree of solubility to be readily distributed through the soil, in an extremely fine state of subdivision, and capable of affording nutriment to the plant under highly favourable conditions."

It is to this further proposition to which we now desire to call special attention, and we may allude first to the assumed loss of the power of spontaneous diffusion through the soil, which is stated by Sibson, in his work on "Artificial Manures," to render the precipitated phosphates inferior in value to soluble acid phosphate. We think that no chemist will doubt that the phosphates in guano are sufficiently soluble to be available for plant food, and precipitated phosphate is certainly more soluble than the earthy phosphates in Peruvian guano. It must be remembered, moreover, when studying the table of solubilities of phosphates, as ascertained by Dr. Voelcker, that these are stated with reference to distilled water, which does not occur in nature, whereas in water containing small percentages of many of the salts, commonly present in the soil, the solubility of phosphates is largely increased. Thus the addition to the water of a trifling amount of ammoniac chloride (1 per cent.) increases the solubility of precipitated calcic phosphate fourfold.

This matter has not then received a due share of attention, for, as we have seen, arguing on the analogy of guano, phosphates, in the precipitated form, are undoubtedly so far soluble as to possess the power of diffusion to an extent amply sufficient for agricultural purposes, and there must be a point, short of perfect solubility, which adequately satisfies all requirements in this respect. A careful consideration of the subject has led us to the conclusion that the effect of phosphoric acid added to the soil, after having been fixed by a suitable base, in a condition sufficiently soluble for every need of the plant, and in a state of subdivision far finer than anything which could be obtained by mechanical means, would be in theory, if not superior, at least equal to that of a similar amount of soluble phosphate, applied to a soil promiscuously, in cases in which it is impossible to predict by what bases the phosphoric acid will be fixed, or even whether it will be fixed at all. Indeed, the foregoing considerations would almost lead us to the belief that the employment of such ready-formed compounds as calcic or magnesian phosphates would be preferable to the haphazard use of soluble phosphoric acid in a super-phosphate.

Chemists in treating of the magnesian phosphates appear to have overlooked the dibasic phosphate and to have conducted their experiments and to have founded their observations mainly, if not entirely, on the behaviour of the far less soluble tribasic phosphate. The freshly-precipitated magnesian phosphate is soluble in about 322 times its weight of pure water, while calcic phosphate, as we have seen when newly precipitated, is soluble to the extent of 5.56 grains per gallon. Both of these salts are therefore much more soluble than the earthy phosphates present in guano. We must not overlook the fact also that although it has not yet received much attention, the magnesia would appear to possess in itself considerable manurial value. A recent French authority assigns to it a value approaching 5s. 8d. per unit, almost three-fourths of the price he sets down for phosphoric acid, and we are convinced from the study of the composition of numerous fertile soils, the ashes of plants, and

recent field-trials, that the day is not far distant when the magnesia will rank as high in a manure as a salt of potash.

Another fact which the foregoing considerations have forcibly brought before us is the value of organic matters, in bringing about the solubility of the phosphates. This is perhaps scarcely within our present scope, but we have mentioned, incidentally, that small quantities of ammonia and carbonic acid, dissolved in the water, produce a very marked effect on the solubility of the phosphates. So valuable is their office in this respect, that it seems a false system to deny that organic matter, when present in a manure, possesses any value whatever. It was formerly the practice with agricultural chemists to allow 1*l.* per ton (2.4*l.* per unit) for organic matter, and we think that the important office which it fulfils in supplying carbonic acid for bringing into solution additional quantities of the phosphates, fully justifies the assignment to it of the above valuation.

We have thus endeavoured to explain the true conditions under which phosphoric acid becomes, in the soil, a source of plant-food. We have shown that there must be a limit to the value of solubility, merely considered as a means of securing diffusion through the soil, because partially soluble salts also possess the property to a degree sufficient for all practical purposes. In conclusion we have claimed for a ready-formed, partially-soluble phosphate, in a finely divided condition, and, in the case of the magnesian phosphate, possessing the property of fixing at the same time a portion of the ammonia, a value at least as great as that of a soluble acid phosphate, which runs the risk of being fixed by iron, or alumina (should lime be deficient in the soil), or, which may sink below the roots of the plants before it is neutralised. We trust we have thus shown a good case for a more liberal valuation of precipitated phosphates, and have indicated, with some measure of success, the reasons for the excellent results that have been recently obtained by the use of manures containing phosphoric acid in this form.

THE ELECTROLYTIC BALANCE OF CHEMICAL CORROSION¹

THIS paper treats of some fundamental points in silver electroplating, and shows how a large amount of the electric power may be wasted by the use of too large a proportion of free potassic cyanide in the plating-solution, or by using the liquid in a heated state.

It is also described a method of ascertaining the degree of energy of chemical corrosion of metals in electrolytes, by means of the strength of electric current per unit of surface necessary to prevent such corrosion; the metals and liquids employed for the purpose in the present research being silver, and solutions of argento cyanide of potassium containing free potassic cyanide. Numerous examples, chiefly in the form of tables, are given of the strength of current required to enter cathodes of a given amount of surface, in order to exactly balance the chemical corrosive effect upon them at atmospheric temperatures, and at higher ones, of solutions of potassic cyanide of various degrees of strength.

The method employed was to take a given solution of cyanide of potassium, pass through it by means of a sheet of platinum anode and a burnished sheet of silver cathode, a weak electric current, and add gradually to the liquid (with stirring) small portions of argento potassic cyanide, until the faintest perceptible deposit of silver occurred. The verge of deposition thus attained was called "the balance point;" and the conditions which determine and influence it, constitute the subject of this research.

The effect of various conditions upon the point of balance of electric and chemical energy were investigated, and the experiments are described. The influences examined were: composition of the liquid, strength of current, size of cathode and density of current, electro-motive force, temperature, ordinary chemical corrosion, nature of the cathode, etc. The circumstances were also investigated which affect the measurement of the current by the method employed in this research, viz. by depositing silver from a solution of argento potassic cyanide; and the sources of error, (and their limit), in that method, are pointed out. The effect of varying the proportions of free potassic cyanide, and of argento potassic cyanide, upon the strength of current at the balance point, are shown in tables of results. The strengths of current just sufficient to prevent all

¹ Abstract of paper by G. Gore LL.D., F.R.S., read before the Birmingham Philosophical Society, Dec. 14, 1882.